Characterization of Mainstem Streams Using Water-Quality Profiles

By Kenneth J. Leib, M. Alisa Mast, and Winfield G. Wright

Chapter E11 of

Integrated Investigations of Environmental Effects of Historical Mining in the Animas River Watershed, San Juan County, Colorado

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Conversion Factors, Definitions, and Abbreviations

Multiply	By	To obtain
inch (in.)	2.54	centimeter (cm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
yard (yd)	0.9144	meter (m)
square mile (mi^2)	2.590	square kilometer (km^2)
gallon (gal)	3.785	liter (L)
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
cubic foot per second per square mile ((ft^3/s)/mi^2)	0.01093	cubic meter per second per square kilometer ((m^3/s)/km^2)
pound per day (lb/d)	0.4536	kilogram per day (kg/d)

Temperature in degrees Celsius (°C) is converted to degrees Fahrenheit (°F) as follows:

$$°F=(1.8\times°C)+32$$

Water year is defined as the 12-month period October 1 through September 30. The water year is designated by the calendar year in which it ends.

Additional Abbreviations

α	the regression coefficient that is the intercept in the regression model
β	constant beta used in hyperbolic transformation
B and B_n	coefficient of explanatory variables in multiple regression
C_Q	constituent concentration in milligrams/liter
DV_1	flushing variable
J_C	first order Julian date transformation
J_D	second order Julian date transformation
J_E	third order Julian date transformation
J_F	fourth order Julian date transformation
X_Q	streamflow in cubic feet
X_h	transformed streamflow
r^2	coefficient of determination
µg/L	micrograms per liter
µS/cm	microsiemens per centimeter at 25° Celsius
mg/L	milligrams per liter

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Abstract

One of the important types of information needed to characterize water quality in streams affected by historical mining is the seasonal pattern of toxic trace-metal concentrations and loads. Seasonal patterns in water quality are estimated in this report using a technique called water-quality profiling. Water-quality profiling allows land managers and scientists to assess priority areas to be targeted for characterization and (or) remediation by quantifying the timing and magnitude of contaminant occurrence.

Streamflow and water-quality data collected at 15 sites in the Animas River watershed study area during water years 1991–99 were used to develop water-quality profiles. Data collected at each sampling site were used to develop ordinary least-squares regression models for streamflow and constituent concentrations. Streamflow was estimated by correlating instantaneous streamflow measured at ungauged sites with continuous streamflow records from streamflow-gauging stations in the basins. Water-quality regression models were developed to estimate concentrations of hardness and dissolved cadmium, copper, and zinc based on streamflow and seasonality. Results from the regression models were used to calculate water-quality profiles for streamflow, constituent concentrations, and loads.

Quantification of cadmium, copper, and zinc loads in a selected stream segment in Mineral Creek (sites M27 to M34) provides an example application of water-quality profiling. The application used a method of mass accounting to quantify the portion of metal loading in the segment derived from uncharacterized sources (sites where no water-quality data have been collected) during different seasonal periods. During May, uncharacterized sources contribute nearly 95 percent of the cadmium load, 0 percent of the copper load (or uncharacterized sources are also attenuated), and about 85 percent of the zinc load at M34. During September, uncharacterized sources contribute about 86 percent of the cadmium load, 0 percent of the copper load (or uncharacterized sources are also attenuated), and about 52 percent of the zinc load at M34. Characterized sources accounted for more of the loading gains estimated in the example reach during September, possibly indicating the presence of diffuse inflows during snowmelt runoff. Regardless of the sources of the loads, the results indicate that metal sources in the Animas River watershed study area may change substantially with season.

Introduction

Seasonal and spatial patterns of toxic metal concentrations and loads are one of the important types of information needed to characterize water quality in streams affected by historical mining. Typically, the concentrations of most dissolved constituents in streams decline during high streamflow and increase during base flow (Anderson and others, 1997). An understanding of when trace-metal concentrations are highest improves the ability of biologists to evaluate the health of aquatic ecosystems. Biologists are interested in periods of highest trace metal concentrations, as aquatic species would be highly vulnerable to acute exposures (hours to a few days) under these field conditions. In contrast, land managers generally are most interested in knowing what areas contribute the largest trace metal loads in order to assess where remediation would be most effective. Because the largest trace metal loads generally occur during periods of high streamflow, and high concentrations and toxicities (Besser and Leib, this volume, Chapter E19) occur during periods of base flow, it is important to characterize seasonal concentration patterns over an entire annual cycle.

Several years of sample collection are needed to adequately characterize an annual water-quality cycle, because wet, dry, and normal years can have dissimilar water-quality patterns. A long-term water-quality database that exists for the Animas River watershed was used as a starting point for quantifying seasonal water-quality patterns at gauged and ungauged sites in the watershed. This database, although extensive, could not provide accurate estimates of annual water-quality cycles due to the gaps between sampling periods. A continuous estimate of water quality, including streamflow and concentration derived from the existing data, was needed. Therefore, select data sets were expanded using linear regression to estimate periods when no data were collected. By this means, a more accurate estimate of the annual range and timing of constituent concentrations and loads could be reported, because uncertainty was reduced when the data set was expanded to include the modeled data. This report summarizes how statistical modeling is used to characterize water-quality conditions in mainstem streams of the Animas River watershed study area as part of a technique for presenting watershed-scale information about areas affected by historical mining.

Purpose and Scope

The purpose of this report is to characterize spatial and seasonal variability of water quality in the Animas River watershed study area in southwestern Colorado, using a technique known herein as water-quality profiling. Water-quality profiling is similar to traditional seasonal water-quality characterization techniques in which solute concentrations and loads are estimated with regression modeling (Searcy, 1959; Cohn and others, 1989; Crawford and others, 1983). In addition, water-quality profiling combines data from multiple sites to provide information about concentrations and loads along the gradient of a stream. Hence, water-quality profiles depict seasonal differences in water quality at multiple sampling locations in one concise and informative graph. Water-quality profiles quantify the timing and extent of contaminant occurrence and can aid land managers and scientists in determining priority areas to be targeted for characterization and possible remediation. Thus, the water-quality profile presents a useful way to package information from large and complicated data sets in a format that is easily interpreted. A description of how this technique has been applied to water-quality data from the Animas River watershed study is included.

The objectives of this report are the following:

- Describe the methods used to derive water-quality profiles
- Compute water-quality profiles for 15 sampling sites in the Animas River watershed for streamflow and concentrations of hardness and dissolved cadmium, copper, and zinc, which are representative of current water-quality conditions in the Animas River watershed study area
- Discuss results of water-quality profiling
- Present an example application of results from water-quality profiling.

Methodology and interpretation in this report are intended to guide future water-quality studies that seek to quantify effects from multiple sources of contamination in varying hydrologic conditions. An understanding of seasonal patterns of hardness could also improve estimates of metal toxicity, because hardness is used to determine regulatory standards for selected constituents. Hardness of water, calculated by summing equivalents of polyvalent cations (primarily calcium and magnesium) and expressed as equivalent concentration of calcium carbonate ($CaCO_3$), is included in many calculations of instream water-quality standards because it can lessen the toxic effects of certain dissolved constituents including cadmium, copper, and zinc.

Description of Study Area

The Animas River watershed study area encompasses about 146 mi^2 of rugged terrain in the San Juan Mountains of southwestern Colorado (U.S. Geological Survey, 1991–2000). Elevations range from 9,200 ft near the town of Silverton, Colo., to nearly 13,900 ft at the summit of Vermilion Peak (fig. 1). The upper part of the Animas River has a channel length of about 15.5 mi upstream from streamflow-gauging station 09359020 (site A72) and an average gradient of about 184 ft/mi. Major tributaries to the upper Animas River are Mineral and Cement Creeks, which represent about 50 percent of the Animas River watershed study area drainage. Climate in the area is characterized by long, cold winters and short (3 to 4 month), cool summers (von Guerard and others, this volume, Chapter B). Average monthly air temperature at Silverton, Colo., ranges from 16° F in January to 55.3° F in July. Precipitation averages 45 in. annually, of which about 70 percent accumulates in a seasonal snowpack between November and April (Colorado Climate Center, 2000). Most of the remaining precipitation falls during monsoonal thundershowers in late summer and early fall. The Animas River watershed study area lies in the Southern Rocky Mountain ecoregion province (Bailey and others, 1994), with much of the area existing above treeline. Areas below treeline typically are vegetated by dense stands of subalpine Engelmann spruce and subalpine fir.

Mine Site Remediation

Mining in the San Juan Mountains has left a legacy of inactive mines as sources of acidic mine drainage (Church, Mast, and others, this volume, Chapter E5). The majority of sites in the Animas River watershed study area have been inventoried, and some priority mines are slated for remediation. Remediation has the potential to change water quality at downstream sampling sites. For this reason, it was necessary to document the completion date and location of remediation projects in the study area. Later in the report, this information will be used for trend analysis to determine which data sets or portions of data sets represent stable water-quality conditions.

Based on the limited number of remediation projects completed at the time this report was written (2000), trends (if any) in water quality were assumed to be related to mined-land remediation done by Sunnyside Gold Corporation. Sunnyside Gold Corporation, through an agreement signed in May 1996 with the Colorado Department of Public Health

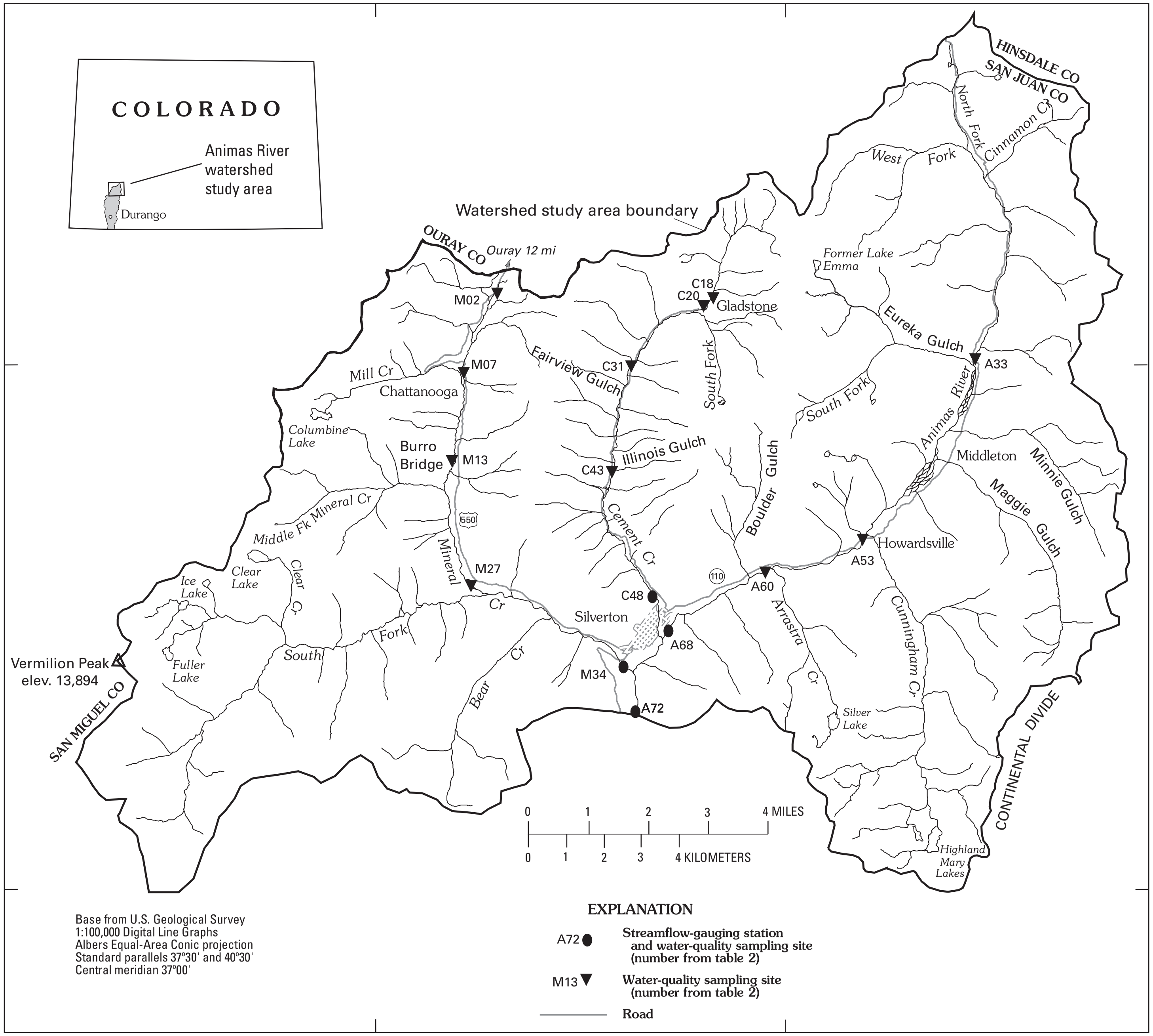

Figure 1. Streamflow-gauging stations and water-quality sampling sites in the Animas River watershed study area.

and Environment, Water-Quality Control Division, closed the valves on bulkhead seals placed in inactive mines in Cement Creek and tributaries to the Animas River and also removed and (or) covered select mine wastes (Colorado Department of Public Health and Environment, 1995). Beginning in 1996, Sunnyside Gold Corporation also treated the majority of streamflow in Cement Creek during periods of base flow between sites C18 and C20 (fig. 1), using settling ponds to precipitate metals in solution. Most of these projects and many other smaller ones were completed in the summer of 1997; however, other maintenance work and mined-land remediation is ongoing in the Animas River watershed study area by both Sunnyside Gold Corporation and an increasing number of Federal and private parties. Completion dates for Federal and private party projects (excluding Sunnyside Gold Corporation) were not compiled and considered in this study because of the small number and small size of each project relative to the Sunnyside Gold Corporation projects. Table 1 lists dates and locations for mined-land remediation projects done by Sunnyside Gold Corporation (Larry Perino, Sunnyside Gold Corporation, written commun., 2000), used in this study to interpret possible trends in water quality.

Data Collection and Data Synthesis

Water-quality data presented in this report were collected by seven groups and government agencies. During water years 1991 to 1999, water-quality data were collected by the Colorado Department of Health and Environment (CDPHE), Sunnyside Gold Corporation (SGC), Colorado Division of Minerals and Geology (CDMG), Colorado River Watch (CRW), and the Bureau of Reclamation (BOR). Water-quality data were also collected by the USGS during water years 1997 to 1999, in cooperation with the Bureau of Land Management (BLM), as part of this study. Data from each group reside collectively in the Animas River Stakeholders Group (ARSG) website located at www.wateinfo.org/arsg/main.html#data.

Water-Quality Sampling Sites

In 1997, fifteen sampling sites on the upper Animas River and its two major tributaries (Cement and Mineral Creeks) were selected for inclusion in this study (table 2). Four of these sites were streamflow-gauging stations with continuous streamflow record (fig. 1). The sites were in the downstream portion of the Animas River watershed study area; two were near the mouths of Cement (C48) and Mineral Creeks (M34) and two were on the Animas River—one upstream from Cement Creek (A68) and the other downstream from Mineral Creek (A72). Continuous streamflow records from these gauged sites were used to estimate streamflow at ungauged sites. These sites also had an extensive record of water-quality data (from 32 to 112 samples). Also, 11 ungauged sites in the middle and upper parts of the Animas River watershed study area were selected because their locations bracketed major mining-related sources of metals and because some water-quality data were already available. Additional water-quality data (Mast and others, 2000; Animas River Stakeholders Group, 2000) were collected at some sites during water years 1997–99 to ensure that sufficient data for statistical modeling were available for all sites.

Sample Collection and Laboratory Analysis

Sample-collection protocols and laboratory analytical methods differed slightly among agencies and groups; however, there was a concerted effort to adopt common

Table 1. Summary of major mined-land remediation projects in the Animas River watershed study area.

[-, not applicable]

Project	Mine No.[1]	Completion date	Downstream sampling sites	Basin
American tunnel bulk-head closure	96	September 9, 1996	C20,C31,C43,C48,A72	Cement Creek.
Cement Creek treatment	-	ongoing	C20,C31,C43,C48,A72	Cement Creek.
Terry tunnel bulkhead closure	120	July 17, 1996	A53,A60,A68,A72	Upper Animas River.
Lead Carbonate and American tunnel mine waste dump removal.	95	Fall 1995	C31,C43,C48,A72	Cement Creek.
Sunnyside Eureka mill tailings removal	164	Fall 1996	A53,A60,A68,A72	Upper Animas River.
Ransom tunnel bulkhead	504	June 1997	A53,A60,A68,A72	Upper Animas River.
Boulder Creek tailings removal	-	June 1997	A68,A72	Upper Animas River.
Gold Prince project	49	September 1997	A33,A53,A60,A68,A72	Upper Animas River.
Longfellow/Koehler project	75, 77	Fall 1997	M02,M07,M13,M27, M34,A72	Mineral Creek.
Pride of the West tailings removal	233	Fall 1997	A53, A60, A68, A72	Upper Animas River.
Mayflower Mill diversion project	221, 510	Fall 1999	A68,A72	Upper Animas River.
Tailings pond surface and ground-water drainage project.	510	December 1999	A68,A72	Upper Animas River.

[1]Church, Mast, and others, this volume, Chapter E5.

Table 2. Descriptive information for sampling sites.

[mi^2, square miles]

Sampling site name	Sampling site No. (fig. 1)	Lat N.; long W.	Drainage area (mi^2)	Percentage of Animas River watershed study area	River mile (distance downstream from respective subbasin headwaters)	Streamflow-gauging station number
Cement Creek upstream from Gladstone	C18	37°53'26"; 107°38'55"	3.0	2.1	2.7	ungauged
Cement Creek near Gladstone	C20	37°53'23"; 107°39'08"	3.1	2.1	2.9	ungauged
Cement Creek downstream from Georgia Gulch	C31	37°52'31"; 107°40'17"	9.44	6.5	4.5	ungauged
Cement Creek downstream from Illinois Gulch	C43	37°50'50"; 107°40'38"	14.8	10.1	6.3	ungauged
Cement Creek at Silverton	C48	37°49'11"; 107°39'47"	20.1	13.8	9.2	09358550
Mineral Creek near headwaters	M02	37°53'40"; 107°42'48"	0.10	0.1	0.15	ungauged
Mineral Creek at Chattanooga	M07	37°52'27"; 107°43'26"	4.4	3.0	1.8	ungauged
Mineral Creek at Burro Bridge	M13	37°51'02"; 107°43'31"	10.4	7.1	3.5	ungauged
Mineral Creek upstream from South Fork Mineral Creek.	M27	37°49'16"; 107°13'08"	20.0	13.7	5.9	ungauged
Mineral Creek at Silverton	M34	37°48'10"; 107°40'20"	52.4	35.9	9.0	09359010
Animas River at Eureka	A33	37°52'45"; 107°33'55"	18.2	12.5	6.2	ungauged
Animas River at Howardsville	A53	37°50'07"; 107°35'52"	57.7	39.5	10.1	ungauged
Animas River near Arrastra Creek	A60	37°49'38"; 107°37'34"	60.0	41.1	12.1	ungauged
Animas River at Silverton	A68	37°48'40"; 107°39'31"	70.6	48.4	14.3	09358000
Animas River downstream from Silverton	A72	37°47'25"; 107°40'01"	146	100	16.0	09359020

sample-collection protocols, compare laboratory analytical methods, and collect concurrent replicate samples for comparison of results among laboratories. A complete description of the methods used for laboratory analysis, data collection, and quality assurance is available in Mast and others (2000) and Leib and others (2003).

Streamflow Regression Models

Streamflow regression models were developed to provide estimated daily-mean streamflow at ungauged sampling sites. The streamflow models were developed by regressing daily-mean streamflow at gauged sampling sites with instantaneous streamflow measured at ungauged sites. Sites C18, C20, C31, and C43 in Cement Creek were correlated to site C48; sites M02, M07, M13, and M27 in Mineral Creek were correlated to site M34; and sites A33, A53, A60, and A68 in the Animas River were correlated to site A72. Sites A33, A53, and A60 were correlated to site A72 rather than site A68 (a gauged site on the Animas River) because the correlation was better at A72.

During water years 1991–99, between ten and twenty streamflow measurements at each ungauged site were obtained during different streamflow conditions. As many as four measurements at each of the ungauged sites were obtained in 1991–96. The rest of the measurements were obtained from 1997 to 1999 with the exception of sites A60, C31, M07, and M13, which were all obtained in 1999. When possible, these measurements were taken monthly during fall and winter and more frequently during snowmelt.

Streamflow regression models were derived using ordinary least-squares (OLS) regression. Each model was evaluated for significance based on the coefficient of determination (r^2), p-values, residual plots, and the standard error of estimate. Values of r^2 less than 0.6 and p-values >0.05 were generally considered an indication of a poor correlation.

Additional information regarding streamflow model selection, including statistical diagnostics, equation form, and model significance, is discussed in Leib and others (2003).The form of the regression equation used for estimating streamflow at ungauged sampling sites is:

$$Y_Q = B(X_Q) + \alpha \qquad (1)$$

where

Y_Q is the streamflow at the ungauged site, in ft^3/s;

B is the slope of the regression line;

X_Q is the streamflow at the gauged site in ft^3/s;

and

α is the y intercept of the regression line.

Water-Quality Regression Models

Water-quality regression models were developed to estimate daily values of hardness and concentrations of dissolved cadmium, copper, and zinc at gauged and ungauged sites. Water-quality data used for regression modeling were obtained during different streamflow regimes at all sampling sites. Constituent concentrations below minimum reporting levels were assigned one-half the value of the minimum reporting level.

Water-Quality Hysteresis

A pattern measured in many streams is a tendency for water of a rising stage to have a considerably higher constituent concentration than water passing a sampling point at an equal flow rate after peak discharge has passed (Hem, 1985). This condition is referred to as "hysteresis" and has been documented in the Animas River watershed study area by Wirt and others (1999) for localized storm runoff events in Cement Creek. Besser and Leib (1999) also observed hysteresis in the upper Animas River and found that concentrations of dissolved zinc and copper, during the rising limb of the snowmelt hydrograph, can be 2 or 3 times those that occur at similar flow rates during the receding portion of the snowmelt hydrograph. In addition, concentrations of dissolved zinc and copper tended to increase during periods of base flow (November–March) with little variation in streamflow. Figure 2 illustrates the hysteretic pattern at A72 for dissolved zinc in water year 1997. This plot illustrates the clockwise progression that dissolved zinc concentration takes throughout the water year. During base flow, concentrations increase despite little or no decrease in streamflow. During the rising limb of the snowmelt hydrograph (April–June), concentrations are diluted; however, concentrations during the rising limb are not as dilute as concentrations on the falling limb of the snowmelt hydrograph (July–October).

The pattern for zinc is typical for other trace metals as well as for other sampling sites in the Animas River watershed study area. Because of hysteresis, it is preferable to correlate constituent concentration with seasonal terms (periodicity) as well as streamflow. Leib and others (2003) have included a discussion of seasonal terms, including transformed Julian date and dummy variables used to characterize outliers which were thought to be related to snowmelt flushing. Outliers, like those shown in figure 3, were characterized with a dummy variable at sites where Julian date transformations were not significant in the regression analysis. These correlations form the foundation from which water quality was estimated.

Model Selection

Variable transformations and equation forms for water-quality models are listed in table 3. Several models contain transformations that were used to improve model utility. For an extensive discussion related to how and why specific transformations are used, see Leib and others (2003). Additional information that addresses the theory and practice of regression analysis is available in Helsel and Hirsch (1992).

Trend Analysis

If transformation of an independent variable did not improve the significance of a given model, a second measure was taken to test for trend in a given data set. Testing for trend in a data set is useful for determining which data points are representative of the condition of interest. The condition of interest for this report is post-remediation (table 1). Trends in a data set may also result from climatic shifts or anthropogenic influences. This study focused on trends that resulted from anthropogenic influences such as impoundments, streamflow diversions, and mined-land remediation. It was assumed that the effect of trend resulting from a change in climate would be negligible on the basis of a period of record of less than 10 years. For the specifics of how trends were analyzed, see Leib and others (2003).

Limitations of Data Analysis

Use of the statistical regression models provided in this report requires adherence to specific guidelines and an understanding of the limitations inherent in each model. Estimates from streamflow and water-quality regression models in this report were only provided after careful consideration of the following guidelines and limitations:

1. Models are site specific.

2. Models with considerable standard error values are less accurate.

3. Data represent water-quality conditions during the period sampled and do not necessarily represent past or future conditions.

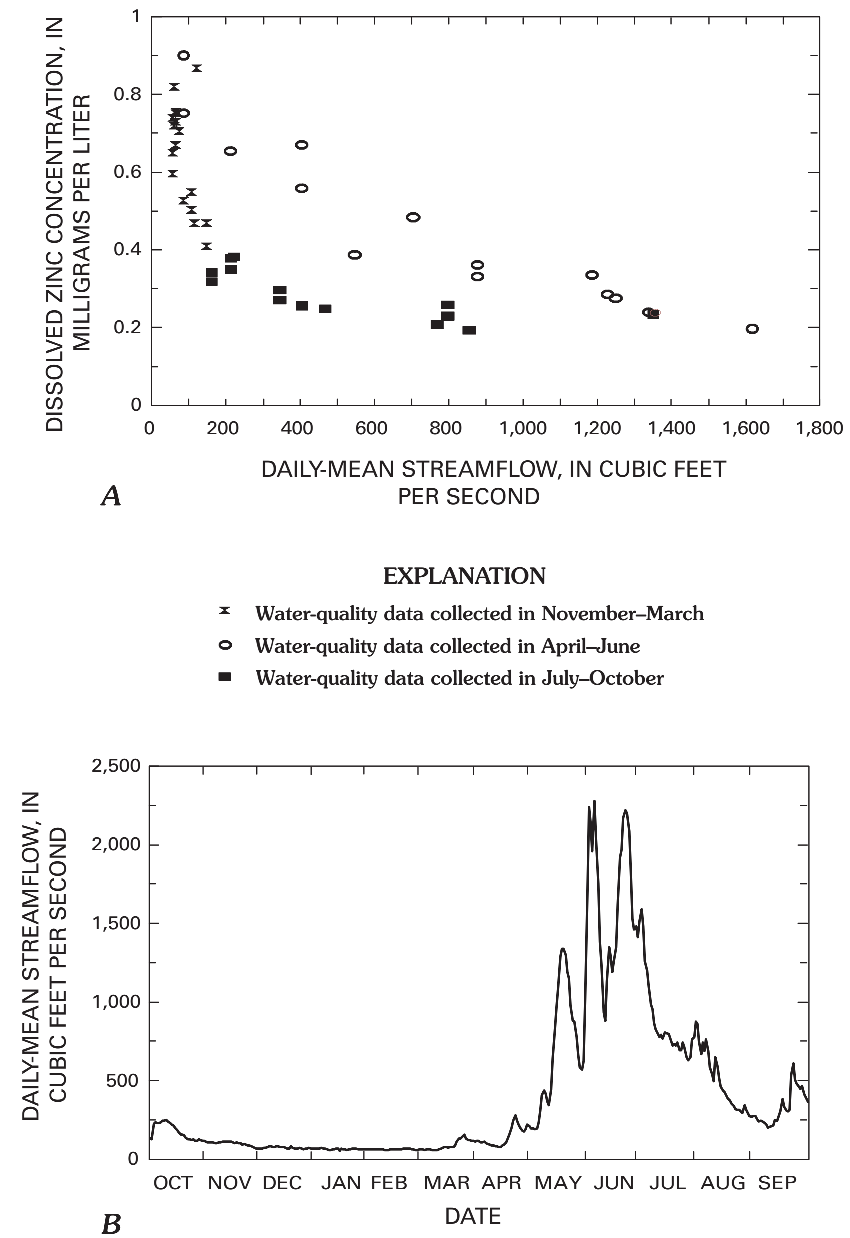

Figure 2. Graphs showing *A*, dissolved zinc concentration related to daily-mean streamflow; *B*, daily-mean streamflow, sampling site A72, water year 1997.

4. Models represent a specific range of estimates which, when exceeded, decreases a model's usefulness.

5. Negative values returned by a water-quality model can occur at the extremes of the estimation range if a model's calibration data set contains extensive data below a constituent's minimum reporting level (MRL). Loading values for negative concentration estimates were reported as one-half the value of the minimum estimate in one annual cycle.

6. Model verification (using sample data collected but not included in model derivations) was done at sites M27 and M34 only for September because of the availability of data.

Although the correlation for gauged and ungauged streamflow is assumed to be constant for the period of record (Leib and others, 2003), values estimated using the streamflow regression models will not always fall within a model's standard error. This situation can occur under certain environmental conditions or if the range of estimation is not considered. Because snow depth, snowpack temperature, and rainfall can vary in a basin with elevation, aspect, and vegetation cover, the onset of runoff from these zones will vary (Dunne and Leopold, 1978). This is especially true in estimation of streamflow at ungauged sites during periods of intense localized rainfall because one or more of the ungauged basins may not experience any rainfall runoff from a rain event that has affected streamflow at a gauged site. When this occurs,

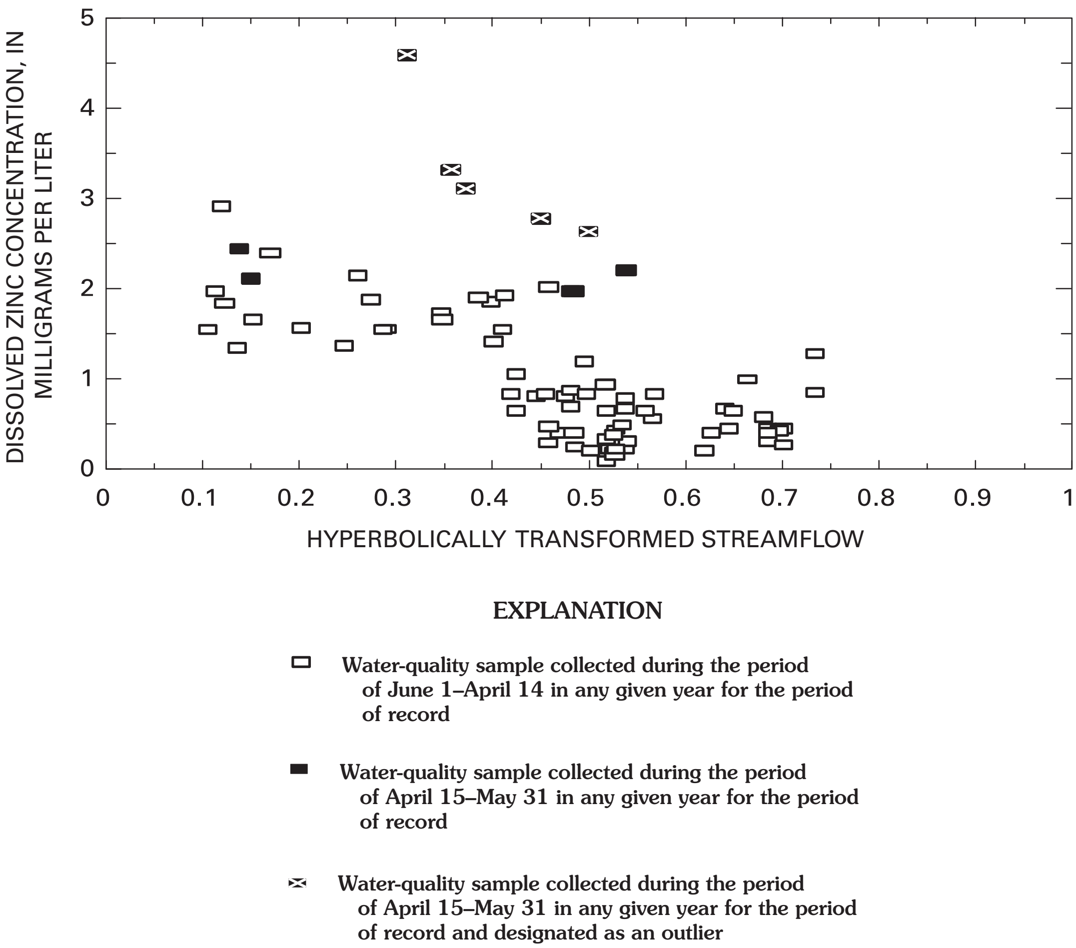

Figure 3. Transformed streamflow related to zinc concentration at site C20 showing presence of outliers.

Table 3. Summary of equation forms used to simulate constituent concentrations at sampling sites.

[β, hyperbolic transformation constant; α, the regression coefficient that is the intercept in the regression model; B and B_n, estimated coefficient of explanatory variables in multiple regression; $DV_{1..n}$, flushing variable(s); J_C, first-order Julian date transformation; J_D, second-order Julian date transformation; J_E, third-order Julian date transformation; J_F, fourth-order Julian date transformation; X_Q, streamflow, in cubic feet per second (ft³/s); X_h, transformed streamflow; C_Q, constituent concentration, in milligrams/liter]

Equation form number	Response variable		Explanatory variables		Equation form
	Variable	Transformation	Variables	Transformation	
3	C_Q	None	X_Q	None	$C_Q = B(X_Q) + \alpha$
4	C_Q	Inverse	X_h	Hyperbolic[1]	$1/C_Q = B(X_h) + DV_{1..n}$
			$DV_{1..n}$	None	
5	C_Q	None	X_h	Hyperbolic[1]	$C_Q = B(X_h) + B_1(J_C) + B_2(J_D) +$
			J_C, J_D, J_E, J_F	Trigonometric[2]	$B_3(J_E) + B_4(J_F) + DV_{1..n} + \alpha$
			$DV_{1..n}$	None	
[3]6	C_Q	Logarithmic	X_h	None	$\log C_Q = B(X_h) + B_1(J_C) + B_2(J_D) +$
			J_C, J_D, J_E, J_F	Trigonometric[2]	$B_3(J_E) + B_4(J_F) + DV_{1..n} + \alpha$
			$DV_{1..n}$	None	

[1]Hyperbolic transformation is $X_h = 1/(1+\beta\{X_Q\})$.

[2]Trigonometric transformation, first order, $J_C = \sin[(\pi(\text{Julian date}))/365]$; second order, $J_D = \text{cosine}[(\pi(\text{Julian date}))/365]$; third order, $J_E = \sin[(\pi(\text{Julian date}))/182.5]$; fourth order, $J_F = \text{cosine}[(\pi(\text{Julian date}))/182.5]$.

[3]Equation form uses a logarithmic transformation that requires a bias correction factor when estimating mean response.

the statistical correlation between gauged and ungauged sites is no longer meaningful. Caution should be used in estimation of streamflow at ungauged sites during rainfall events. The authors were aware of this problem and therefore chose to report only monthly loads, thus avoiding possibly sizable errors that could result from their estimating daily loads during periods of rainfall runoff. Also, the timing of snowmelt runoff (lag time) will differ at each ungauged sampling site because snowpack at higher elevations or on northern aspects is usually the last to melt, and south-facing, low-elevation basins usually melt early. Estimates made for ungauged sites using the water-quality models could not be adjusted to account for differences in timing of snowmelt runoff because continuous streamflow data were not available.

Seasonality of Water Quality in the Animas River Watershed Study Area

Water-Quality Profiles

Using the streamflow and water-quality regression models, the authors calculated water-quality profiles for the 15 sampling sites. Three profiles were calculated depicting seasonal fluctuations in streamflow, constituent concentration, and constituent load. Streamflow profiles were developed by, first, an estimation of daily-mean streamflow at each sampling site. At ungauged sites, the streamflow regression models were used to estimate daily-mean streamflows, and at gauged sites, the continuous streamflow record was used. The daily-mean streamflows were used to calculate mean-monthly flows that were then plotted as streamflow profiles by basin. Daily-mean streamflow values were used in the water-quality models to estimate daily-mean constituent concentration. The daily-mean constituent concentrations were used to calculate average-monthly concentrations, and results were then plotted at each sampling site as a concentration profile. Daily-mean constituent loads were calculated from the product of the daily-mean constituent concentration and daily-mean streamflow. The resulting loads were then averaged to produce mean-monthly loads and plotted as loading profiles. Concentration and loading profiles were not developed at sites where water-quality regression models were not statistically significant ($p > 0.05$).

Streamflow regression-model coefficients for each ungauged site are listed in table 4. Each streamflow model uses equation 1 ("Streamflow Regression Models" section). Water-quality regression-model coefficients and the appropriate equation from table 3 are listed in table 5. All streamflow and water-quality regression models used to estimate water-quality profiles were significant at the 5 percent level ($p < 0.05$) and generally showed constant variance throughout the range of prediction in residual plots. Water-quality regression models were not considered significant enough for estimation of cadmium and copper at all sampling sites in Cement Creek basin and for zinc at sites C31, C43, and C48.

The range of estimation provided for each site in tables 4 and 5 refers to the range of streamflow encountered when samples were collected. Estimates made using the streamflow and water-quality regression models outside the range of estimation will be less reliable than those made within the limits of model calibration.

Water-quality profiles for selected months (February, May, June, July, and September) were plotted to illustrate seasonal increases or decreases in concentration and load between sampling sites in an average year. February was selected to represent base flow; May, June, and July were selected to represent snowmelt runoff (spring and summer); and September was selected to represent the monsoonal season (late summer and fall). Note that the following sections use the monthly means (figs. 6, 9, and 12) for May, June, and July to represent snowmelt runoff, whereas the base flow and monsoonal periods (February and September respectively) use only one monthly mean each from the water-quality profiles. This was done to account for the extreme variability in water quality during the runoff period.

Table 4. Summary of streamflow regression model coefficients and diagnostics at sampling sites.

[α, the regression coefficient that is the intercept in the regression model; r^2, the coefficient of determination; X_Q, explanatory variable streamflow, in cubic feet per second (ft^3/s), at streamflow-gauging station]

Sampling site (fig. 1)	Range of estimation[1] (ft^3/s)	α	Coefficients for explanatory variable X_Q (ft^3/s)	r^2	Standard error of estimate (ft^3/s)
			Cement Creek[2]		
C18	8.5–239	–1.26	0.15	0.75	3.5
C20	8.5–202	–1.14	.206	.87	2.35
C31	12–174	–2.41	.53	.98	4.4
C43	17–123	–0.12	.76	.99	2.23
			Mineral Creek[3]		
M02	19–903	0.0	0.002	0.83	0.27
M07	19–550	0.0	.099	.84	8.3
M13	32–550	0.0	.21	.94	8.8
M27	19–400	6.13	.28	.96	7.8
			Upper Animas River[4]		
A33	57–1,500	–7.4	0.12	0.96	10.7
A53	57–1,500	0.0	.35	.95	31.3
A60	83–1,500	0.0	.40	.94	40.7
A68	56–2,040	0.0	.42	.99	24.2

[1]Estimation range applies to the explanatory variable of streamflow (X_Q) from corresponding streamflow-gauging station.

[2]The explanatory variable (X_Q) is obtained from streamflow-gauging station number 09358550.

[3]The explanatory variable (X_Q) is obtained from streamflow-gauging station number 09359010.

[4]The explanatory variable (X_Q) is obtained from streamflow-gauging station number 09359020.

Table 5. Summary of water-quality regression model coefficients and diagnostics at sampling sites.

[β, constant used in hyperbolic transformation; α, the regression coefficient that is the intercept in the regression model; B and B_n, coefficient of explanatory variables in multiple regression; DV_1, flushing variable; J_C, first-order Julian date transformation; J_D, second-order Julian date transformation; J_E, third-order Julian date transformation; J_F, fourth-order Julian date transformation; mg/L, milligrams per liter; X_Q, streamflow, in cubic feet per second (ft³/s); X_h, transformed streamflow; r^2, the coefficient of determination; --, explanatory variable was not used in the regression model or was not applicable]

Sampling site	Equation form from table 3	Range of estimation (ft³/s)	β	α	$B..B_n$: X_Q (ft³/s)	X_h	J_C	J_D	J_E	J_F	DV_1	r^2	Standard error of estimate (mg/L)	Bias correction factor
Hardness—Cement Creek														
C18	5	0.047–32	0.55	43.3	--	171	--	--	--	--	[c]93.9	0.82	36.7	--
C20	5	1.5–35.3	10	154	--	19,429	--	--	--	--	--	.90	120	--
C31	5	7.2–98.0	1	46.1	--	4,485	--	--	--	--	--	.95	40.3	--
C43	5	12.6–95.5	0.1	30.6	--	900.5	--	--	--	--	--	.91	43.2	--
C48	5	12.0–329	10	64.8	--	62,397	--	--	--	--	--	.91	49.4	--
Dissolved zinc—Cement Creek														
C18	5	0.047–32	1.33	2.55	--	2.86	0.32	0.65	--	--	[b]0.62	0.61	0.95	--
C20	5	1.5–35.3	0.24	1.66	--	–1.39	.061	–0.40	--	--	[a]1.44	.73	0.538	--
Dissolved cadmium—Mineral Creek														
M02	5	0.02–2.1	100	0.0	--	2.23	--	--	--	--	--	0.92	0.115	--
M07	5	.17–65.5	0.41	.0	--	0.03	--	--	--	--	--	.90	.002	--
M13	5	3.5–123	.05	.0	--	.0071	--	--	--	--	--	.95	.001	--
M27	5	9.1–134	.07	.0007	--	.0041	--	--	--	--	--	.64	.0005	--
M34	5	15–863	.019	.0005	--	.0012	0.0003	0.0000	0.0001	–0.0002	--	.65	.0003	--
Dissolved copper—Mineral Creek														
M02	5	0.02–2.1	10	–1.07	--	60.4	--	--	--	--	--	0.93	5.25	--
M07	5	17–65.5	0.50	0.0	--	1.19	--	--	--	--	--	.81	0.095	--
M13	5	3.5–123	1.0	.020	--	0.452	--	--	--	--	--	.78	.018	--
M27	5	9.1–134	.05	–.002	--	.173	--	--	--	--	--	.80	.019	--
M34	5	15–964	.05	–.005	--	.087	0.0096	0.0002	--	--	--	.76	.01	--
Hardness—Mineral Creek														
M02	5	0.02–2.1	10	75.9	--	382.7	--	--	--	--	--	0.80	60.3	--
M07	5	17–65.5	0.31	23.05	--	59.4	--	--	--	--	--	.92	5.5	--
M13	5	3.5–123	1.5	37.7	--	1,552	--	--	--	--	--	.91	25.5	--
M27	5	9.1–134	1.1	34.3	--	4,196	--	--	--	--	--	.94	32.6	--
M34	5	15–752	.05	38.9	--	417	--	--	--	--	--	.95	17.0	--
Dissolved zinc—Mineral Creek														
M02	5	0.02–2.1	12	0.0	--	176	--	--	--	--	--	0.98	4.06	--
M07	5	17–65.5	0.25	–.014	--	4.44	--	--	--	--	--	.98	0.15	--
M13	5	3.5–123	.07	.005	--	1.88	--	--	--	--	--	.94	.120	--
M27	5	9.1–134	.04	.038	--	0.985	--	--	--	--	--	.91	.070	--
M34	5	15–863	.025	.078	--	.510	0.049	0.037	–.024	–0.038	--	.91	.051	--

Table 5. Summary of water-quality regression model coefficients and diagnostics at sampling sites.—Continued

Sampling site	Equation form from table 3	Range of estimation (ft³/s)	β	α	$B..B_n$							r^2	Standard error of estimate (mg/L)	Bias correction factor
					X_a (ft³/s)	X_h	J_C	J_D	J_E	J_F	DV_1			
					Dissolved cadmium—Upper Animas River									
A33	5	1.15–177	0.005	0.0	--	0.0026	--	--	--	--	--	0.95	0.0005	--
A53	3	14.3–505	--	7.0E-04	2.36E-06	--	--	--	--	--	--	.66	.0003	--
A60	4	26.2–680	100	1,089	--	5.05E+04	--	--	--	--	[f]–310	.60	.006	--
A68	6	8.5–880	.004	–3.34	--	0.822	0.064	–0.009	--	--	[f]0.147	.64	.0014	1.0
A72	5	55.5–2,340	.004	.001	--	.0013	.00048	.00005	–0.00006	–0.0002	[b]3.0E–4	.74	.0003	--
					Dissolved copper—Upper Animas River									
A33	5	1.15–177	0.2	0.0051	--	0.01711	0.0062	–0.0015	--	--	[d]0.017	0.83	0.005	--
A53	5	14.3–505	0.01	0.0	--	.0032	--	--	--	--	[f].005	.88	.0015	--
A60	5	26.2–680	1.0E-06	–28.42	--	28.42	–.0011	–.0061	--	--	[f].015	.92	.0019	--
A68	5	8.5–880	--	.003	--	--	.001	–.0003	–0.001	–0.0001	.0033	.62	.002	--
A72	5	55.5–2,340	--	.011	--	--	.0075	.0057	.0028	–.00126	--	.80	.003	--
					Hardness—Upper Animas River									
A33	5	1.15–177	0.1	57.2	--	49.3	–0.187	21.0	13.0	–1.34	--	0.98	4.6	--
A53	5	14.3–505	.01	27.2	--	122	--	--	--	--	--	.95	6.6	--
A60	5	26.2–680	.0078	23.3	--	122	--	--	--	--	--	.91	9.0	--
A68	5	8.5–880	.013	45.1	--	144	7.24	10.0	--	--	--	.97	8.0	--
A72	5	55.5–2,340	.02	48.8	--	520	8.77	9.61	–1.22	–6.58	--	.93	23.2	--
					Dissolved zinc—Upper Animas River									
A33	5	1.15–177	0.035	0.307	--	0.253	--	--	--	--	--	0.65	0.051	
A53	5	14.3–505	.0009	.0	--	.291	--	--	--	--	[d]0.042	.98	.038	--
A60	5	26.2–680	.002	.0	--	.303	--	--	--	--	[f].076	.97	.044	--
A68	5	8.5–1,050	.007	.0	--	.834	0.188	–0.028	--	--	[e].140	.90	.188	--
A72	5	55.5–2,340	.01	.249	--	.598	.152	.0298	–0.0267	–0.0592	--	.87	.07	--

[a]A value of 1 is assigned to the flushing variable during the period April 15 to May 31.

[b]A value of 1 is assigned to the flushing variable during the period April 1 to May 31.

[c]A value of 1 is assigned to the flushing variable during the period January 1 to March 31.

[d]A value of 1 is assigned to the flushing variable during the period May 1 to May 31.

[e]A value of 1 is assigned to the flushing variable during the period April 1 to June 30.

[f]A value of 1 is assigned to the flushing variable during the period May 1 to June 30.

Cement Creek

Estimates of seasonal water quality in Cement Creek basin were calculated for sites C18, C20, C31, C43, and C48. Regression models were statistically significant for streamflow and hardness at all sampling sites. Models at two sites (C18 and C20) were statistically significant for zinc, whereas no models were significant for cadmium and copper at any sites in Cement Creek. Significant models for hardness and zinc had r^2 values ranging from 0.61 to 0.95 (table 5).

The streamflow profile for sites in Cement Creek is shown in figure 4. The profile indicates that base flow in Cement Creek ranges among sampling sites from less than 1.0 ft^3/s at C18 to about 13 ft^3/s at C48. Peak snowmelt runoff generally occurs in June and ranges from about 24 ft^3/s at site C18 to 150 ft^3/s at C48. Estimated streamflow from Cement Creek basin is generally from about 10 to 22 percent of the total streamflow at site A72 for any given month. About 30–40 percent of the streamflow at site C48 originates between sites C20 and C31 during snowmelt runoff. Average-annual streamflow from Cement Creek basin is about 42 ft^3/s or a yield of about 2.1 $ft^3/s/mi^2$.

A trend detected at site C20 indicated that a decrease in streamflow occurred in 1996. This change may have resulted from the September 1996 closure of the American tunnel bulkhead near Gladstone, Colo. (table 1). The trend was most apparent during base-flow conditions (fig. 5). A trend during high flow was not apparent, possibly due to streamflow measurement error, which is often more prevalent during high stage. No trends in streamflow were detected at C48; therefore, all streamflow measurements were used in streamflow model development at sites C31 and C43. Data for samples collected before September 1996, however, were not used to derive models at site C20.

Concentration and loading profiles for hardness and zinc estimated using the Cement Creek water-quality models are shown in figure 6. The highest monthly concentration of hardness (1,280 mg/L) was estimated at site C20 during base flow and the lowest (55 mg/L) was estimated at site C18 during snowmelt runoff. The largest increases in hardness concentration were estimated between sites C18 and C20 throughout the year, with an average increase during base flow of about 1,000 mg/L and an increase during snowmelt runoff of about 130 mg/L. The large increase in hardness concentration in this reach most likely results from lime applications at the Sunnyside Gold Corporation water-quality treatment facility (Larry Perino, Sunnyside Gold Corporation, written commun., 1999). Hardness concentrations in Cement Creek were lowest at site C18 and highest at site C20 year around.

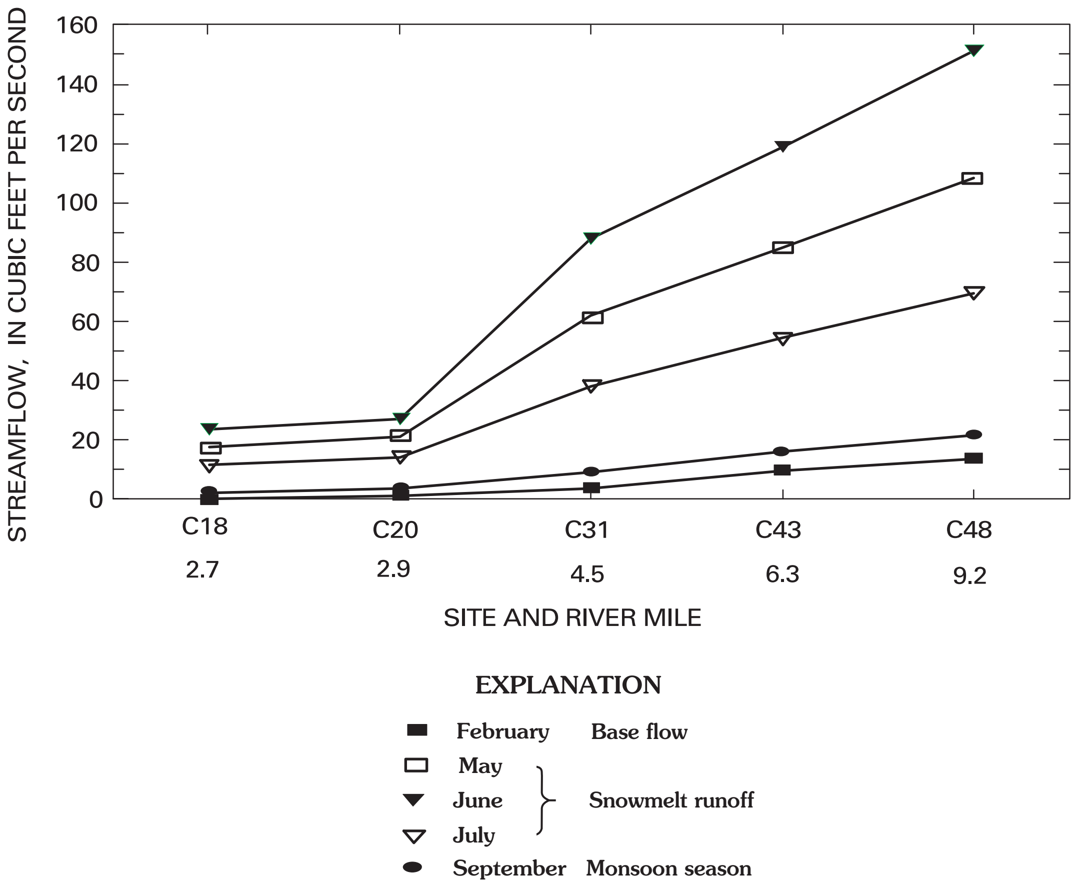

Figure 4. Streamflow profile for Cement Creek basin.

The largest hardness load in Cement Creek basin was estimated at site C48 during snowmelt runoff (87,000 lb/d), and the smallest was estimated at site C18 during base flow (1,000 lb/d). Among the sites, the largest increase in hardness load during base flow occurred between sites C18 and C20 (about 10,000 lb/d); however, loading between sites was fairly consistent regardless of location at this time. During snowmelt runoff, the largest increase in hardness loading to Cement Creek also occurred between sites C18 and C20 (about 29,300 lb/d).

A flushing variable was retained in the hardness water-quality model after stepwise regression at site C18 for the period of January 1 to March 31 (DV_1, table 5). Estimation of concentrations at this site during this period used a value of 1 assigned to the flushing variable. The reason for the increase in hardness concentration during this period is not known, but outliers were apparent in *xy* plots of the measured sample data much like the outliers for zinc were apparent at C20 (fig. 3).

A decreasing trend in hardness concentration was detected at sites C20 and C48. This trend correlates to the period when the American tunnel bulkhead was closed in September 1996 (table 1). Figure 7 shows the apparent shift in the correlation of streamflow with hardness concentration that occurred during this time period. As a result of trend detection for hardness, data collected before September 1996 were not used to derive water-quality regression models for hardness at sites C20, C31, C43, and C48.

The highest monthly concentration of zinc (5.4 mg/L) was estimated at site C18 during base flow, and the lowest (0.40 mg/L) was estimated at site C20 during the same period (fig. 6). Concentrations at site C18 were higher during base flow than during snowmelt runoff, but concentrations at site C20 tended to be lower during base flow relative to snowmelt runoff concentrations. The decrease most likely results from the effect of the water-quality treatment plant located between sites C18 and C20. The plant treats most of the water in Cement Creek during base flow (winter) but does not have the capacity to treat all the streamflow during snowmelt runoff. Both sampling sites retained a flushing variable for either April through May or May (DV_1, table 5).

The largest and smallest monthly loads of zinc were estimated at site C20 during May (330 lb/d) and February (2.4 lb/d). The largest increase in zinc loading between the two sites occurred in May (about 50 lb/d); however, this amount is small relative to the loading that occurred upstream from C20, which ranges from 90 to 100 percent (depending on the season) of the total load at C20.

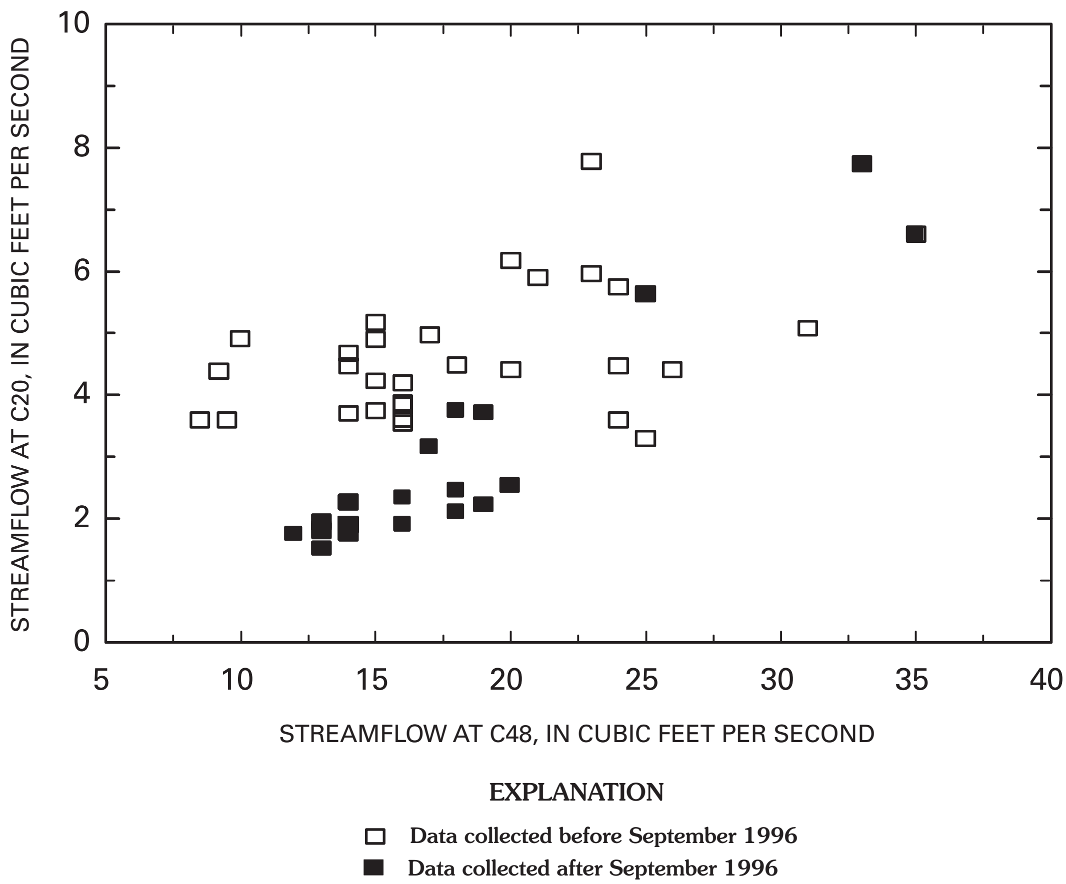

Figure 5. Streamflow data before and after American tunnel bulkhead closure in September 1996.

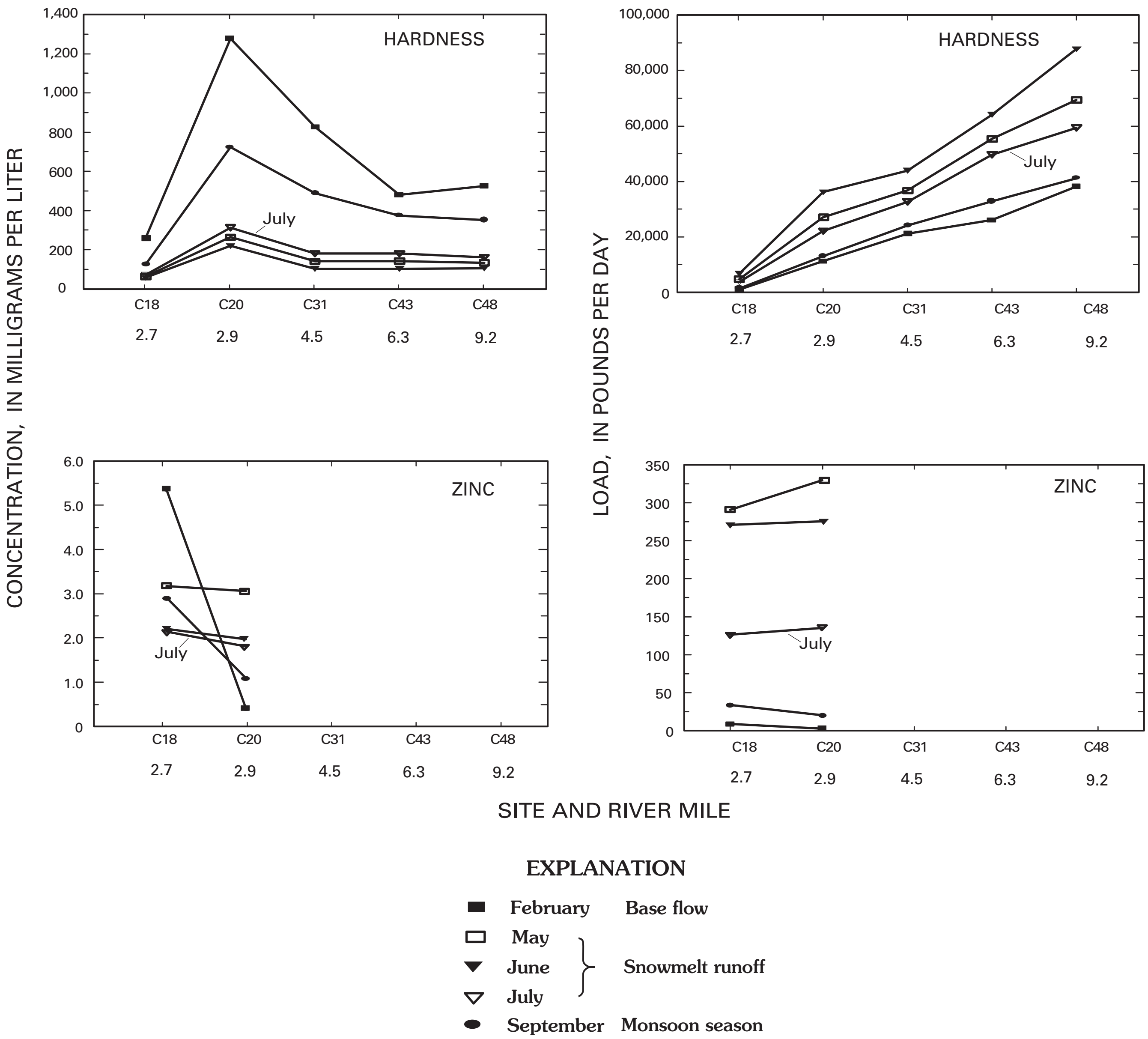

Figure 6. Water-quality profiles for hardness and dissolved zinc at Cement Creek sampling sites.

Mineral Creek

Streamflow and water-quality profiles in Mineral Creek basin were calculated for sites M02, M07, M13, M27, and M34. Regression models at all sites in Mineral Creek were statistically significant for streamflow, hardness, cadmium, copper, and zinc; r^2 values ranged from 0.64 to 0.98 (table 5). Streamflow profiles for Mineral Creek basin are shown in figure 8, and concentration and loading profiles for hardness and metals are shown in figure 9.

The streamflow profile for Mineral Creek indicates that base flow ranges from less than 0.1 ft^3/s at M02 to about 21 ft^3/s at M34. Peak snowmelt runoff generally occurs in June and ranges from about 1.0 ft^3/s at site M02 to 460 ft^3/s at M34. Estimated streamflow from Mineral Creek basin is generally about 32–52 percent of the total streamflow at A72, of which about 43–70 percent originates between sites M27 and M34. Average-annual streamflow draining Mineral Creek basin is about 120 ft^3/s (yield of 2.2 ft^3/s/mi^2).

The highest monthly concentration of hardness (335 mg/L) was estimated at site M02 during February, and the lowest (26 mg/L) was estimated at site M07 in June. Hardness values are highest at site M02 throughout the year with concentrations that ranged from 100 to 335 mg/L; however, concentrations at site M27 approach 335 mg/L during base flow.

The largest monthly hardness load in Mineral Creek was estimated at site M34 during June (139,000 lb/d), and the smallest was estimated at site M02 in February (86 lb/d). The

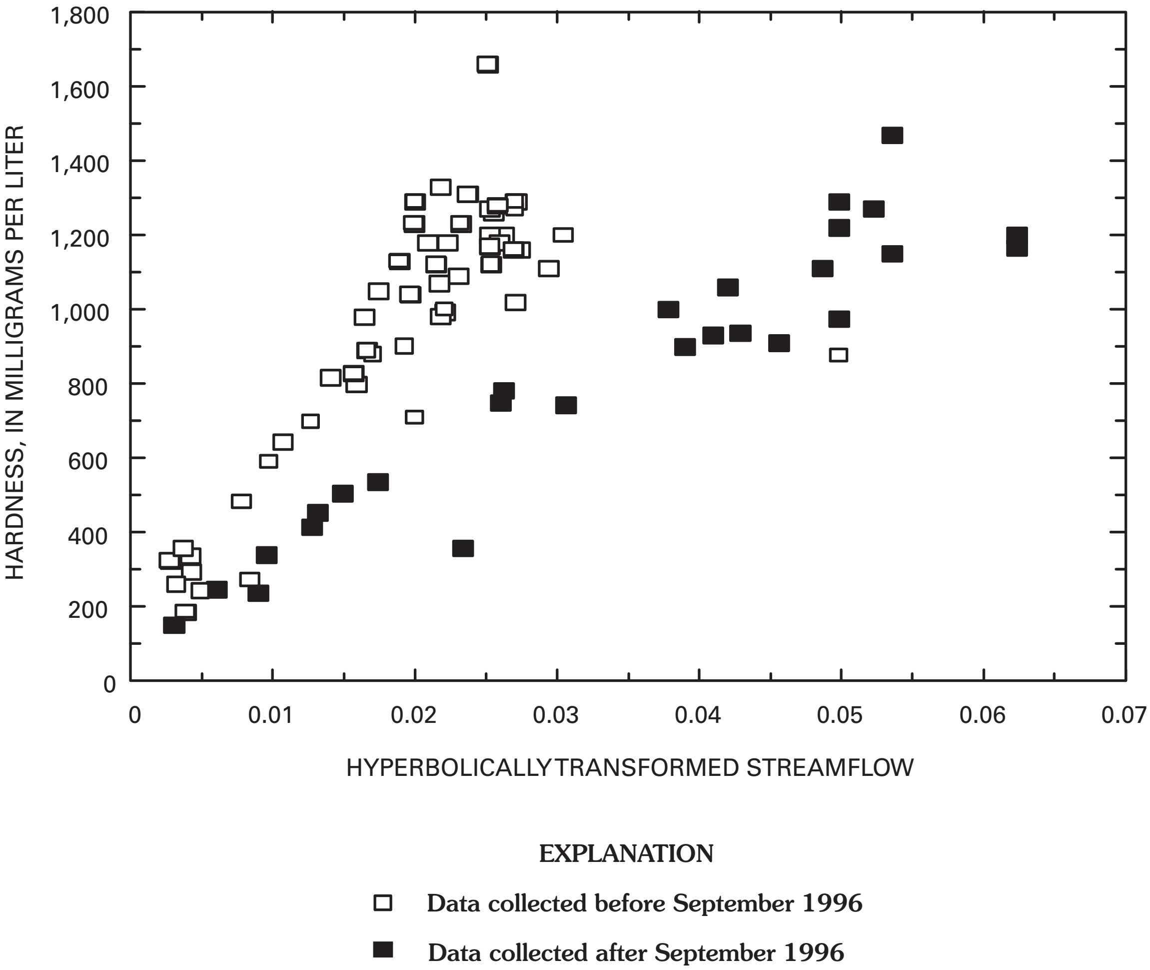

Figure 7. Hardness data at site C20 before and after American tunnel bulkhead closure in September 1996.

largest increase in hardness loading to Mineral Creek during base flow occurred between sites M13 and M27 (16,500 lb/d), and the largest increase in loading during snowmelt runoff occurred between sites M27 and M34 (71,000 lb/d). Hardness loads from Mineral Creek are generally about 27–37 percent of the hardness load at A72 for any given month.

The highest monthly concentration of cadmium (0.39 mg/L) was estimated at site M02 in February, and the lowest (0.0006 mg/L) was estimated at site M34 in July. Cadmium concentrations were highest at M02 throughout the year with concentrations that ranged from 0.020 to 0.39 mg/L. Concentrations decrease considerably at downstream sampling sites where estimates ranged from 0.0006 mg/L at M34 to 0.016 mg/L at M07.

The largest monthly load of cadmium in Mineral Creek was estimated at site M34 during June (1.8 lb/d), and the smallest (0.06 lb/d) was estimated at site M02 in February. The largest increase in cadmium loading to Mineral Creek during base flow occurred upstream from site M02 (0.10 lb/d) and between sites M02 and M07 (0.08 lb/d). The largest increase in loading during snowmelt runoff occurred between sites M27 and M34 (0.87 lb/d). The estimates indicate that seasonal cadmium loads at the mouth of Mineral Creek basin (M34) account for about 15–25 percent of the total cadmium load at A72.

The highest monthly concentration of copper (39.8 mg/L) was estimated at site M02 in February, and the lowest (0.0004 mg/L) was estimated at site M34 in August (not shown). Copper concentrations were highest at M02 throughout the year with concentrations that ranged from 3.0 to 39.8 mg/L. Concentrations decrease considerably at downstream sampling sites where estimates ranged from 0.0004 mg/L at M34 to 0.6 mg/L at M07.

The largest monthly load of copper in Mineral Creek was estimated at site M02 during July (24.5 lb/d), and the smallest (1.1 lb/d) was estimated at site M34 in July. The largest increase in copper loading to Mineral Creek during base flow occurred upstream from site M02 (10 lb/d) and between sites M13 and M27 (4.5 lb/d). The largest increase of loading during snowmelt runoff primarily occurred upstream from site M02 (23 lb/d) and between sites M13 and M27 (3.3 lb/d). Stream reaches M02 through M13 and M27 to M34 showed

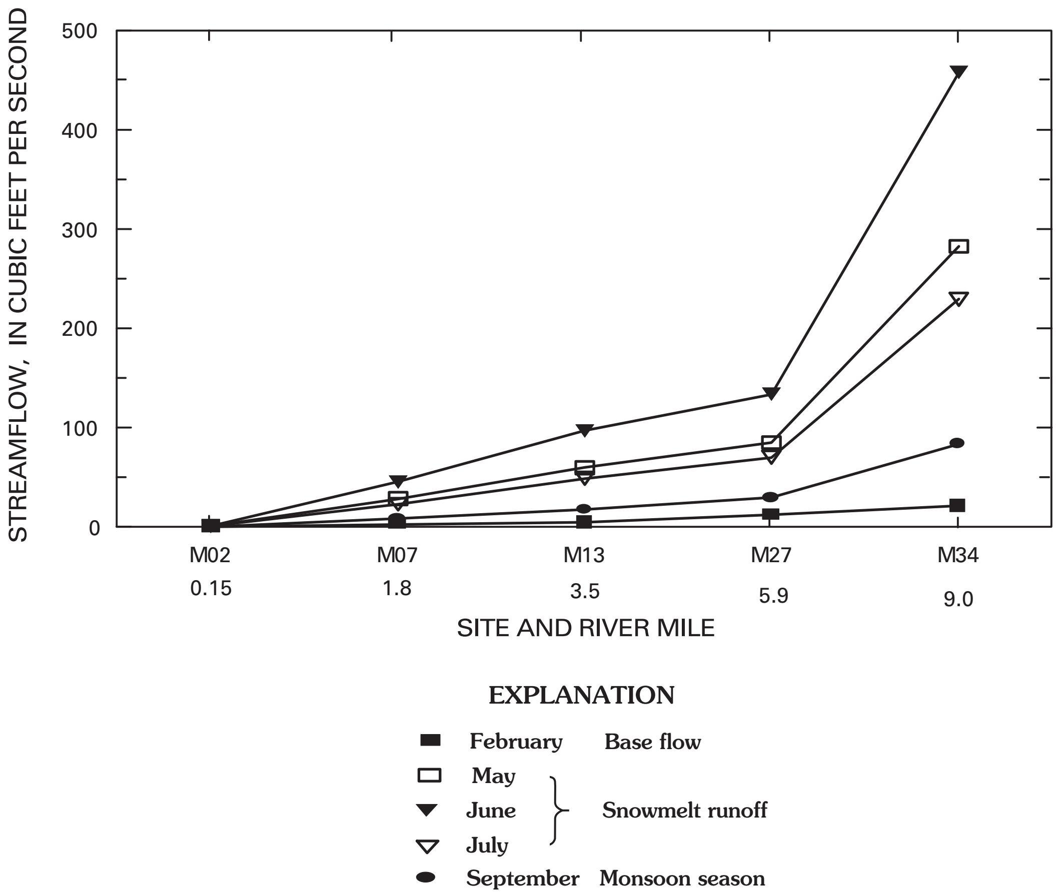

Figure 8. Streamflow profile for Mineral Creek basin.

no net loading increases during any part of the year. This does not imply that no loading is occurring in these sections but may indicate an attenuation of copper load that exceeds the rate of loading from sources draining into these stream segments. Estimates indicate that seasonal copper loads at M34 account for about 31–65 percent of the load at A72 for any given month.

The highest monthly concentration of zinc (112 mg/L) was estimated at site M02 during February, and the lowest (0.05 mg/L) was estimated at site M34 in June. Zinc concentrations were highest at M02 throughout the year with estimates that ranged from 13.0 mg/L to 112 mg/L. Concentrations decrease considerably at downstream sampling sites where estimates ranged from 0.05 mg/L at M34 to 2.9 mg/L at M07.

The largest monthly load of zinc in Mineral Creek was estimated at site M34 during May (220 lb/d), and the smallest was estimated at site M02 in February (28 lb/d). The largest increase in zinc loading to Mineral Creek during base flow occurred between sites M13 and M27 (11.2 lb/d), and the largest increase in loading during snowmelt runoff occurred between sites M27 and M34 (39.5 lb/d). Models indicate that seasonal zinc loads at M34 account for about 10–27 percent of the load at A72 for any given month.

Decreasing trends in trace-metal concentrations were measured for zinc and copper at site M34 (fig. 10). These trends correlate to the period when the Longfellow/Koehler project was completed in fall 1997 (table 1). The project consisted of the removal of dump material near sampling site M02 that was exposed to runoff during spring snowmelt. As a result of trend detection, data collected before October 1997 were not used to derive water-quality regression models for zinc and copper at sites M02, M07, M13, and M27.

Upper Animas River

Streamflow and water-quality profiles in the upper Animas River basin were calculated for sites A33, A53, A60, A68, and A72 (figs. 11, 12). Site A72, located downstream of sites C48 and M34, was included so that the combined loading from Cement and Mineral Creeks could be quantified and compared to sites upstream from A68. Inclusion of A72 also provided an indirect estimate of the effects of Cement Creek to the Animas River. Recall that direct estimates of Cement Creek loading were not calculated because of the insignificance of the trace-metal water-quality models.

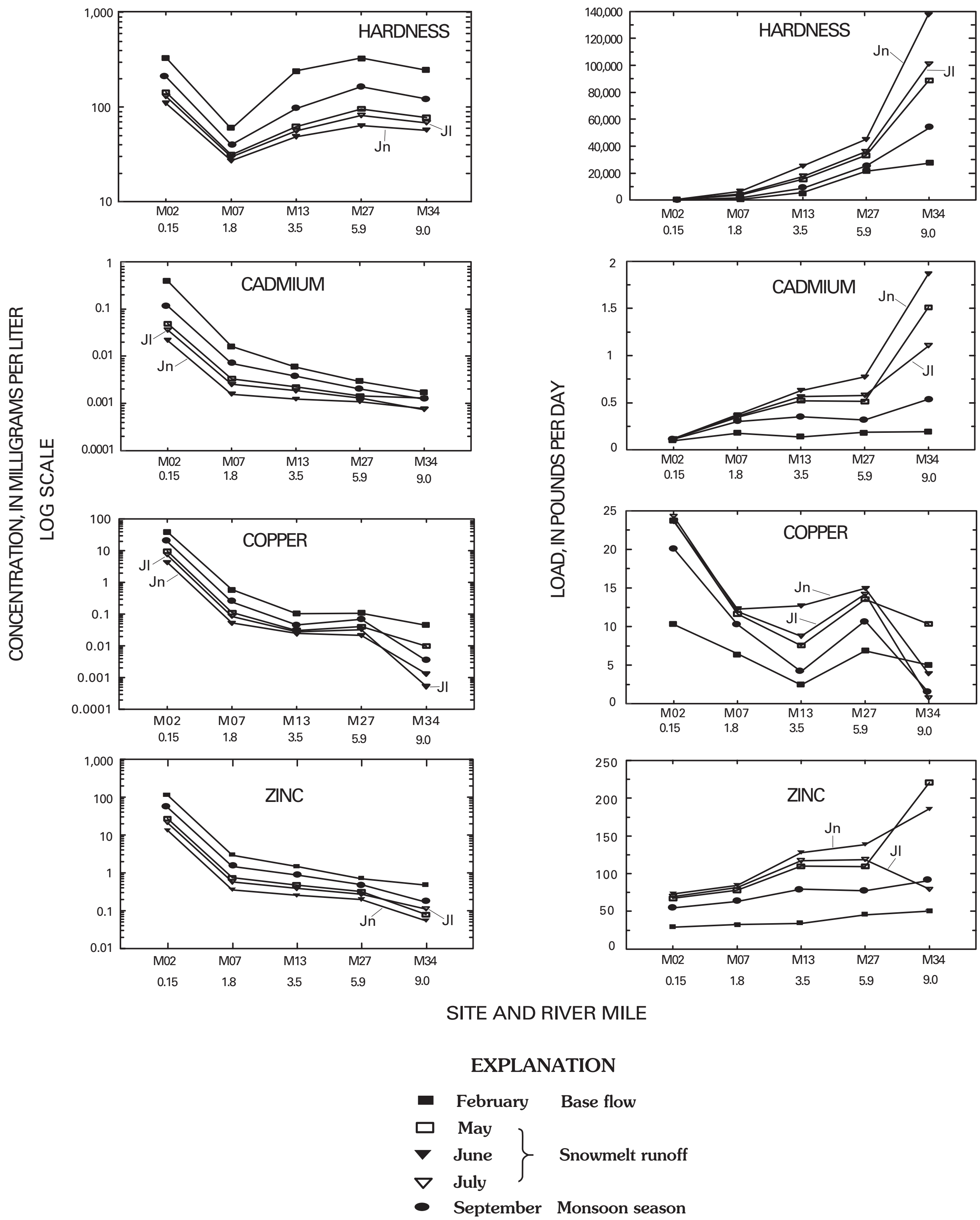

Figure 9. Water-quality profiles for hardness and dissolved cadmium, copper, and zinc at Mineral Creek sampling sites. Jn, June; Jl, July.

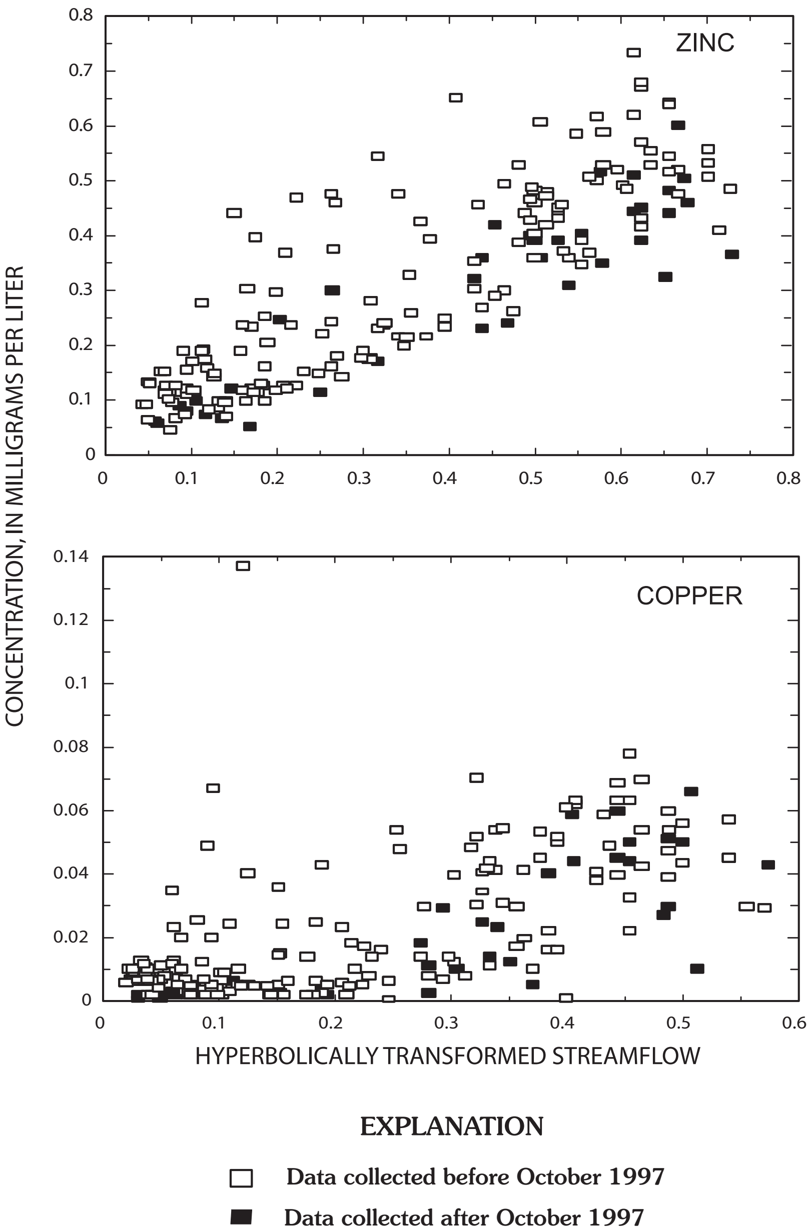

Figure 10. Trace-metal concentrations at site M34 before and after Longfellow/Koehler project was completed in October 1997.

Regression models at all sites in the upper Animas River basin (including A72) were statistically significant for streamflow, hardness, cadmium, copper, and zinc. These models had r^2 values that ranged from 0.60 to 0.98 (table 5). Streamflow profiles for the upper Animas River basin are shown in figure 11, and concentration and loading profiles for metals are shown in figure 12.

Two sites on the upper Animas River (A68 and A72) had large enough data sets to test for trends; however, no trends were detected for hardness or trace metals. This finding indicates that site A72 does not show any measurable effect from the various remediation projects performed in Mineral and Cement Creeks. This does not indicate that no effect has resulted from remediation but only that no effect was measured. Further water-quality monitoring of this site may be necessary to detect subtle trends in concentration that are occurring over an extended period of time.

The streamflow profile for the upper Animas River indicates that base flow ranges among sampling sites from about 0.5 ft^3/s at A33 to about 63 ft^3/s at A72. Peak snowmelt runoff generally occurs in June and ranges from about 140 ft^3/s at site A33 to 1,200 ft^3/s at A72. Estimated streamflow from the upper Animas River basin is generally about 41–42 percent of the total streamflow at A72, of which about 55–83 percent originates between sites A33 and A53. Average-annual streamflow draining the upper Animas River basin (A68) is about 126 ft^3/s (yield of 1.8 $ft^3/s/mi^2$).

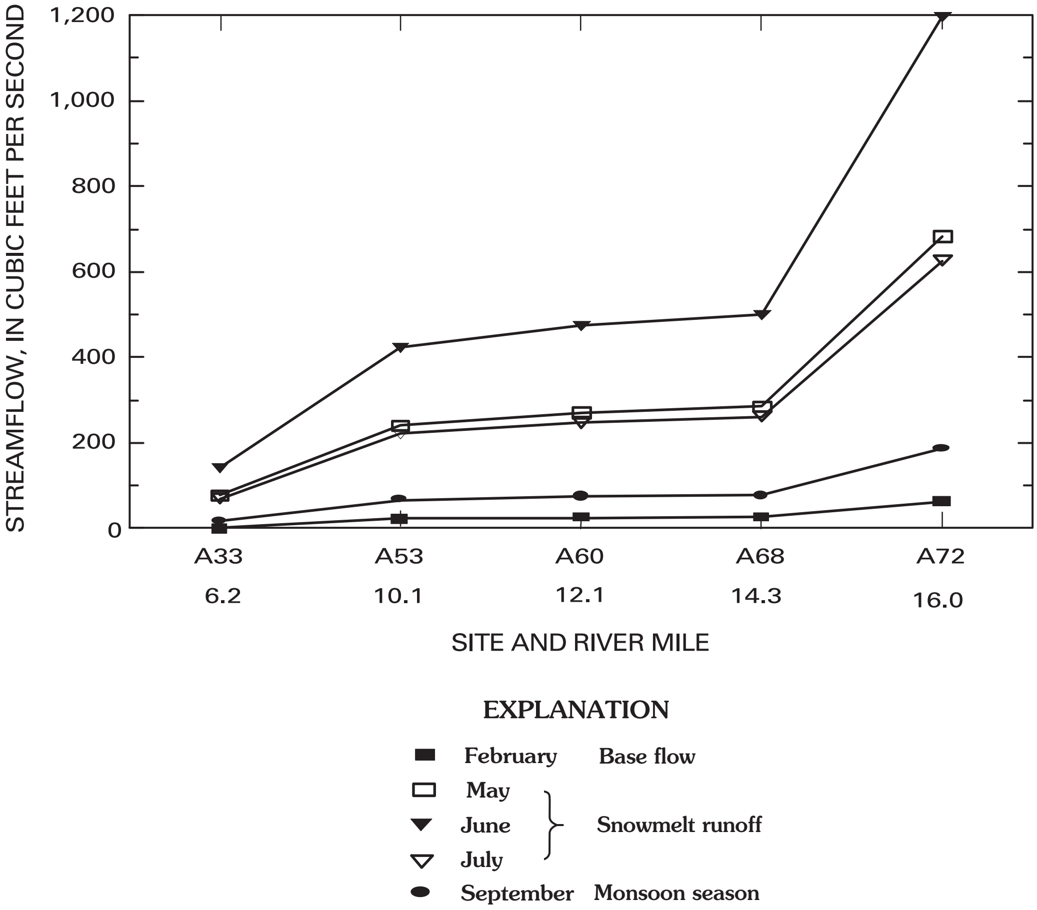

Figure 11. Streamflow profile for upper Animas River.

The highest monthly concentration of hardness (291 mg/L) was estimated at site A72 in January (not shown), and the lowest (30.0 mg/L) was estimated at site A33 in June (fig. 12). Water-quality models estimated hardness concentrations that showed dilution during snowmelt runoff and concentration during base flow. At site A72 in January (not shown), estimated concentrations of hardness were approximately 150–180 mg/L higher than concentrations at other sampling sites in the upper Animas River basin despite the increase in streamflow; however, in May, concentrations at all sampling sites were within 35.0 mg/L of one another. This finding indicates the presence of hardness sources in Mineral and Cement Creeks, which could be important to aquatic habitat during base flow. The decrease in hardness detected at C20 did not noticeably alter the correlation of hardness and streamflow at A72 based on results from the trend testing performed for this study; however, additional portal closures along Mineral or Cement Creeks could theoretically increase stream toxicities in receiving waters if additional hardness sources are eliminated.

The largest monthly load of hardness in the upper Animas River was estimated at site A72 during June (375,000 lb/d), and the lowest (1,450 lb/d) was estimated at site A33 in February. The largest increase in loading in the Animas River during base flow and during snowmelt runoff occurred between sites A68 and A72 at 75,500 lb/d (base flow) and 187,000 lb/d (snowmelt runoff). Sources in the A68 to A72 stream segment contribute from about 59 to 76 percent of the average-monthly hardness load estimated at A72. Approximately two-thirds of the load in the A68 to A72 stream reach originates from Mineral Creek basin during snowmelt runoff, and two-thirds originates from Cement Creek during base flow.

The highest monthly concentration of cadmium (0.0031 mg/L) was estimated at site A72 during the month of April (not shown), and the lowest (0.0007 mg/L) was estimated at site A53 in January and February. Detection limits reported by the USGS for 1997–99 samples in the upper Animas River for cadmium were lower than those of Cement and Mineral Creeks because analysis was done using graphite furnace atomic absorption spectroscopy. The lower detection limit improved the significance of the cadmium models because the majority of cadmium concentrations would have otherwise been below detection limits and therefore estimated. This decision was based on information gained in Mineral Creek and the awareness of low concentrations from preexisting data.

A flushing variable was retained in the cadmium water-quality model after stepwise regression for May 1 through June 30 at sites A60 and A68 and for the period of April 1 to May 31 at site A72 (DV_1, table 5). Estimation of concentrations at this site during this period used a value of 1 assigned to the flushing variable.

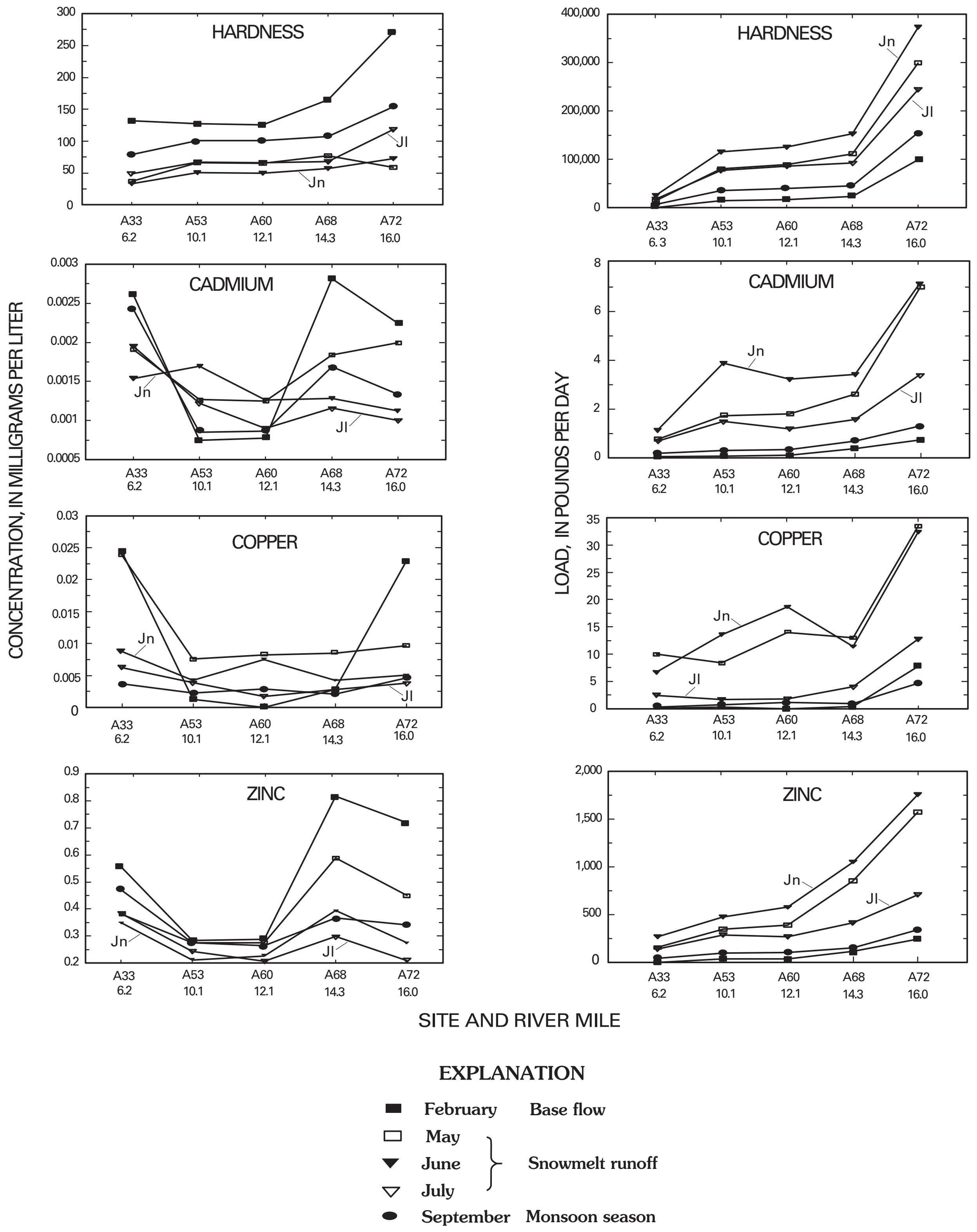

Figure 12. Water-quality profiles for hardness and dissolved cadmium, copper, and zinc at Animas River sampling sites. Jn, June; Jl, July.

The cadmium model at site A53 (and to a lesser extent A60) indicates a positive relation between cadmium and streamflow, which produced the highest cadmium concentration (0.0017 mg/L) in June and lowest (0.0007 mg/L) in February. The Sunnyside Eureka Mill downstream from site A33 (AMLI mine site # 55; Church, Mast, and others, this volume), located between sites A33 and A53, supplied huge quantities of tailings to the river at rates from 50 to 4,700 times greater than the natural production of sediments from hillslopes (Vincent and others, 1999). The presence of mill tailings in the flood plain may explain the positive relation of cadmium concentration to streamflow, because higher streamflow will tend to flush areas of the flood plain that are dry during base flow. Water-quality models for other sites estimated cadmium concentrations that were more dilute during snowmelt runoff than during base flow.

The largest load of cadmium in the upper Animas River was estimated at site A72 during June (7.0 lb/d), and the lowest (0.03 lb/d) was estimated at site A33 in February. The largest increases in cadmium loading in the Animas River during base flow and during snowmelt runoff occurred between sites A68 and A72 at 0.45 lb/d (base flow) and 7.6 lb/d (snowmelt runoff). Loss of cadmium load between sites A53 and A60 may be a result of attenuation in this segment. Models indicate that cadmium loads at the mouth of the upper Animas River basin (A68) account for about 25–53 percent of the load at A72 for any given month.

The highest monthly concentration of copper (0.024 mg/L) was estimated at site A33 during February, and the lowest (0.001 mg/L) was estimated at site A60 in February. Copper models at all sites showed a dilution of copper concentration during snowmelt. The dilution at each site, with the exception of site A72, was preceded by an initial flush of higher copper concentrations in May. The highest concentrations of copper in the upper Animas River typically occurred at the same sampling sites year around. During base flow, the models estimated the highest concentrations of copper at site A33 (0.024 mg/L) and A72 (0.023 mg/L); during snowmelt runoff the highest concentrations of copper (0.023 mg/L) occurred at site A33. During the monsoon season, models at site A60 estimated concentrations (0.0044 mg/L) that approached those of A33 (0.0047). The higher concentrations at A60 during the monsoon season may be occurring as a result of rainfall runoff from Arrastra Creek, the location of several historical mill sites and mines where copper ore was processed.

Flushing variables were retained in several copper water-quality models after stepwise regression for the month of May at site A33, the period of May 1 to June 30 at sites A53 and A60, and April 1 to May 31 at site A68 (DV_1, table 5).

The largest load of copper in the Animas River was estimated at site A72 during May (33 lb/d), and the lowest (0.25 lb/d) was estimated at site A33 in February. The largest increase in copper loading in the Animas River during base flow and during snowmelt runoff occurred between sites A68 and A72 at 7.5 lb/d (base flow) and 16.7 lb/d (snowmelt runoff). Moderate gains in load (5.2 lb/d) during snowmelt runoff also exist between A33 and A60. Estimates from models indicate that seasonal copper loads at A68 are generally about 5–39 percent of the load at A72 for any given month and that the lowest percentages occur during base flow.

The highest monthly concentration of zinc (0.90 mg/L) was estimated at site A68 during April (not shown), and the lowest (0.21 mg/L) was estimated at site A60 in July. Models estimated zinc concentrations that showed dilution during snowmelt runoff and concentration during base flow.

The largest load of zinc in the Animas River watershed study area was estimated at site A72 during June (1,750 lb/d), and the smallest (1.1 lb/d) was estimated at site A33 in February. The largest increase in zinc loading among sites during base flow and snowmelt runoff occurred between A68 and A72 at 125 lb/d (base flow) and 570 lb/d (snowmelt runoff); however, about 40–60 percent of the average-monthly zinc load estimated at site A72 for any given month originated upstream from site A68. Thus, roughly half of the zinc loading at site A72 appears to be coming from Cement and Mineral Creeks and the other half from sources upstream of site A68. The largest increases in zinc loading upstream from A68 occurred either between A33 and A53, or between A60 and A68 throughout the year.

Application of Water-Quality Profiling in Mineral Creek

Water-quality profiles not only provide information about seasonal streamflow, concentration, and load on a watershed scale, but also provide information from which to compare contaminant source loads to instream loads. This comparison is important because undetected contaminant sources (such as diffuse inputs) may be indicated when quantified contaminant sources do not account for the total instream load. To demonstrate this, an example application from Leib and others (2002), which illustrates how contaminant loading can be characterized, is summarized herein.

The example stream segment is defined by sampling sites M27 and M34 (fig. 1) in the Mineral Creek basin. This segment was selected based on the availability of source characterization data and because of the large downstream loading increases in May and June for cadmium and zinc (fig. 9). Changes in load were calculated from the Mineral Creek loading profiles and then compared to loading calculations from contaminant sources, which were obtained from seasonal mine-site characterization studies (Animas River Stakeholders Group, 2000; Mast and others, 2000). Monthly samples from Mast and others (2000) were used to calculate instantaneous loads from the characterized sources in the example reach.

The example stream segment had source characterization data collected at five mine adits during high streamflow (May) and the relatively lower flows of the monsoon season (September). These mine adits represent the majority of mining sources in the stream segment; however, other diffuse sources such as in-stream waste-rock piles and ground-water contributions exist (Kimball and others, this volume).

From the Mineral Creek loading profile, on average during May, net loads of cadmium, copper, and zinc were 1.0 (±0.49) lb/d, –3.1 (±1.52) lb/d, and 111 (±55.4) lb/d (fig. 9), indicating a net gain for cadmium and zinc, and a net loss of copper, along the stream segment. Error estimates for the net loading values were reported as ±one standard deviation of the estimated net loading for the given month. Total characterized source loads in May, computed using the source characterization data for each constituent, indicated that the load discrepancy was about (1) –0.44 to –1.42 lb/d for cadmium, (2) 5.17 to 2.14 lb/d for copper, and (3) –40.6 to –151 lb/d for zinc. The negative load discrepancies indicated that other sources contributed possibly substantial amounts of cadmium and zinc in the M27 to M34 stream segment during May, whereas the positive load discrepancy for copper indicated that attenuation was taking place. Taking the average loading discrepancy estimate from the above ranges for each metal indicated that the uncharacterized sources contributed nearly 95 percent of the cadmium load, 0 percent of the copper load (or uncharacterized sources are also attenuated), and about 85 percent of the zinc load at M34.

For September, net mean monthly loads of cadmium, copper, and zinc were estimated to be 0.22 (±0.12) lb/d, –9.3 (±0.27) lb/d, and 13.8 (±10.5) lb/d (fig. 9), indicating a net gain in cadmium and zinc load, and a net loss of copper along the stream segment. Total characterized source loads in September indicated that the load discrepancy ranged from (1) –0.07 to –0.31 lb/d for cadmium, (2) 9.6 to 9.06 lb/d for copper, and (3) 5.01 to –16.0 lb/d for zinc. The negative load discrepancy range for cadmium indicated that other sources were contributing metals along the stream segment during September. The positive loading-discrepancy range for copper indicated an attenuation of metals from characterized sources. Zinc is more difficult to define based on the positive and negative range; however, an average value for the loading discrepancy (–5.49) indicated that additional sources were present in the stream reach during September. Taking the average loading discrepancy estimate for each constituent indicated that the uncharacterized sources contributed about 86 percent of the cadmium load, 0 percent of the copper load (or uncharacterized sources were also attenuated), and about 52 percent of the zinc load at M34.

Further characterization of the M27 to M34 segment may help explain where uncharacterized loads of cadmium and zinc emanate from, especially during snowmelt runoff. The results indicate that these contributions may be diffuse, because the majority of surface-water sources were thought to have been accounted for. Other surface-water sources may exist, however, and there is likely some degree of flushing of attenuated metals. It also appears likely that diffuse sources of copper are not the main source type for copper in the M27 to M34 stream reach. Regardless of where these metals emanate from, mass accounting with loading profiles indicates that metal sources in the Animas River watershed study area may change substantially with season.

Summary

Multi-agency collaborative efforts are being made to assess the effects of historical mining on water quality in the Animas River watershed. Included in these efforts is the U.S. Department of the Interior's Abandoned Mine Lands Initiative. As part of this initiative, the U.S. Geological Survey has provided technical assistance in support of Federal land-management agencies actions to improve water quality in contaminated stream systems associated with former hard rock mining activities. One of the important types of information needed to characterize water quality in streams affected by historical mining is the seasonal pattern of toxic trace-metal concentrations and loads. These patterns were estimated with a technique called water-quality profiling.

Streamflow and water-quality data collected at 15 sites in the Animas River watershed study area during water years 1991–99 were used to develop water-quality profiles. Data collected at each sampling site were used to develop ordinary least-squares regression models for streamflow and water quality. Results from the regression models were used to calculate water-quality profiles for streamflow and select constituent concentrations and loads.

Trends in streamflow and water quality were detected at three locations. A decreasing trend in streamflow was detected at site C20, which may have resulted when the American tunnel bulkhead was closed in September 1996. Data at sites C20 and C48 indicated a decrease in hardness concentrations, which also corresponds to the period when the American tunnel was closed. Data collected at site M34 indicated a decreasing trend for concentrations of copper and zinc, which correspond to the period when the Longfellow/Koehler project was completed in fall 1997.

Hardness estimates at all sampling sites in the Animas River watershed study area indicated that concentrations were generally highest in Cement Creek and lowest in the upper Animas River. At sampling sites in each basin, estimated hardness concentrations varied dramatically during base flow and moderately during snowmelt runoff.

Contributions of hardness loading to Cement Creek were highest between sites C18 and C20 during snowmelt runoff; however, loading contributions were fairly proportional the rest of the year among sites. The largest increases of hardness load in Mineral Creek were estimated to be occurring between sites M27 and M34 during snowmelt runoff and sites M13 to M27 during base flow. The largest increases of hardness loads in the upper Animas River occurred between sites A68 and A72 during base flow and snowmelt runoff.

Cadmium concentrations and loads estimated in Mineral Creek and the upper Animas River were generally higher at Mineral Creek sites; however, concentrations at site A68 exceeded those estimated at site M34 throughout the year. Model estimates at site A53 showed a positive relation of cadmium concentration to streamflow. Flushing of cadmium at sampling sites in the upper Animas River was readily apparent from the models and raw data, whereas flushing of cadmium in Mineral Creek was less extensive.

The largest increase of cadmium load in Mineral Creek was estimated between sites M27 and M34 during snowmelt runoff. Cadmium loads in the upper Animas River were largest between sites A68 and A72 throughout the year.

Copper concentrations estimated for Mineral Creek and the upper Animas River indicated that concentrations were significantly higher at Mineral Creek sites. Estimates of copper concentration at upper Animas River sampling sites were generally highest in May as a result of flushing, but concentrations in Mineral Creek were highest during the later part of the base flow period.

The largest increases of copper load in Mineral Creek were estimated to be occurring upstream from site M02 and between sites M13 and M27 throughout the year. The largest increases of copper load in the upper Animas River occurred between sites A68 and A72 and to a lesser extent between A33 and A60 during snowmelt runoff.

In Cement Creek basin (C18 and C20), the highest concentrations of zinc were estimated at site C18 throughout the year. Concentrations at site C18 were highest during base flow, whereas concentrations at site C20 were lowest during this period. This may be a result of water-quality treatment at the water-quality treatment plant located between sites C18 and C20. The plant treats most of the water in Cement Creek during base flow (winter) but does not have the capacity to treat all the streamflow during snowmelt runoff. Zinc concentrations estimated for Mineral Creek and the upper Animas River indicated that concentrations in Mineral Creek decrease in a downstream fashion, whereas in the upper Animas River, concentrations increase substantially between sites A60 and A68, despite increases estimated by the streamflow profile. Zinc concentrations in Mineral Creek were not elevated during snowmelt by flushing events, but zinc concentrations in the upper Animas River showed this effect.

The largest zinc load in Cement Creek was estimated to be occurring upstream of site C18 throughout the year. Between C18 and C20, decreases in zinc load were estimated during base flow. The largest increases of zinc load in Mineral Creek were between sites M27 and M34 and upstream from site M02 during snowmelt runoff. The largest increases of zinc load during base flow and snowmelt runoff in the upper Animas River occurred between sites A68 and A72; however, loading of zinc upstream from A68 accounts for approximately 40–60 percent of zinc load at A72.

Quantification of cadmium, copper, and zinc loads in a stream segment in Mineral Creek (M27 to M34) was presented as an example application of water-quality profiling. The application used a method of mass accounting to quantify the portion of metal loading in the segment derived from uncharacterized sources during different seasonal periods. During May, uncharacterized sources contributed nearly 95 percent of the cadmium load, 0 percent of the copper load (or uncharacterized sources were also attenuated), and about 85 percent of the zinc load at M34. During September, uncharacterized sources contributed about 86 percent of the cadmium load, 0 percent of the copper load (or uncharacterized sources were also attenuated), and about 52 percent of the zinc load at M34. Characterized sources accounted for more of the loading gains estimated in the example reach during September, possibly indicating the presence of diffuse inflows during snowmelt runoff. Regardless of where the metals emanate from, the results indicate that metal sources in the Animas River watershed study area may change substantially with season.

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